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Synthesis of Al Doped ZnO by Sol-Gel Method for CO_2 Gas Sensing

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***Abstract*—Al doped ZnO is sensitive to many gases like CO, CO2, H2S etc. Al doped ZnO thin film is synthesized by various methods like RF magnetron sputtering, CVD, spray pyrolysis, hydrothermal, Sol-gel etc. This paper discusses the synthesis of Al doped ZnO on a glass substrate by Sol-Gel method. The electrical properties, gas sensing characteristic of prepared thin film of Al doped ZnO was studied. The sensor response was investigated for CO2 gas at varoius temperatures. The results show that the Al doped ZnO thin film is sensitive to CO2 in a particular temperature range i.e. 50æ%C to 300æ%C**.

***Index Terms*—Thin film, CO2 Sensor, Sol-gel method.**

I. Introduction

Gas sensors are manufactured by various techniques, material and phenomenon. But sensor should be smaller and cheaper than the devices used currently. ZnO has good electrical and optical properties. There are many other techniques to develop ZnO film, such as RF magnetron sputtering, CVD, Spray pyrolysis, sol-gel process, hydrothermal. The main advantages of Sol-gel method are homogeneity on molecular level, easy procedure, cost effective, film quality control by controlling the doping concentration. Al doped ZnO film exhibits low resistivity.

A. Literature Survey

A. Literature survey has been carried out on various techniques to develop thin films for CO2 gas sensing.[1] Y. Huo and A.H.Jayatissa (2012) have used precursor-1 containing Zinc acetate, isopropyl alcohol and MEA as stabilizer and precursor-2 containing Zinc nitrate, isopropyl alcohol, glycol and using Aluminium nitrate as dopant in both precursors for preparing Al doped ZnO films by Sol-Gel method. The undoped ZnO film shows high resistance as compared to the doped ones. The response of gas is given by

$$S= (Ra-Rg)/ (Ra) * 100 \ldots\ldots\ldots\ldots (1)$$

where Ra is resistance of sensor in air and Rg is resistance in presence of target gas. This film showed increase in conductivity with increase in temperature. The films were used to check the H2 gas response and it shows increase in sensing response with increase in H_2 concentration from 400 to 2000ppm. Also from results precursor-1 have more promising results than precursor-2. Films were prepared with different Al doping concentration and 3at% doped film shows optimal sensor performance. [2] V. Musat and P.Vilarinho (2004) have prepared Al doped ZnO thin film by dip coating as deposition method. Sol-gel mixture was prepared using Zinc acetate, aluminium chloride, MEA as sol stabilizer and 2-methoxiethanol as solvent. Increase in Al content as doping material increases the electrical conductivity. The film with 2 wt% shows lowest resistivity (1.33 _ 10"3cm). Corning 1737 glass was used as substrate and the films gives very good transmittance (80-90%) within visible wavelength region. [3] S. D. Shinde and Jain (2012) used hydrothermal method to prepare ZnO nanorods. They were made of various shapes and sizes by using zinc acetate and cetyltriammonium bromide (CTAB). Thick films of these nanorods were prepared by screen printing technique. This thick film shows maximum response to H_2S gas at room temperature (30æ%C) and ethanol at 330æ%C. Also for other gases its response has been checked. [4] G. M. Wu and C.Lu (2011) used chemicals such as, Zinc acetate,aluminium-nitrate,2-propanol, ethanolamine, acetic acid, methyl acetate and ethyl acetate to prepare sol-gel mixture. Dip coating was used for coating the glass substrate. RF magnetron sputtering is also used to prepare Al doped ZnO films in N_2O/Ar ambient gas. They showed increased resistivity with the N_2O partial pressure ratio. The sol-gel Al doped ZnO film prepared by preheating at 500æ%C shows sheet resistivity of 1.8_10$_5$/sq. Its optimal transmittance was high in visible range. Film doped with 2 at% Al shows hexagonal wurzite structure with (002) orientation of crystal. [5] A. Patil and R.Borse (2011) made Al doped ZnO thick films by screen printing technique. These films show significant sensitivity to CO_2 gas at 250æ%C. Various Al concentrations were used on aluminium substrate to check sensitivity to CO_2 gas. 10 wt % Al shows good results. Butyl Carbitol acetate (BCA) was used as vehicle to make paste of ZnO: Al material. The (10 wt% Al) films are oxygen difficent and hence this leads to semiconducting behaviour of the material. Not only for CO_2 gas but it shows response to various gases like NH_3,H_2S, Ethanol, LPG, NO_2. The sensitivity for CO_2 gas increases up to 500 ppm and then increase is slow. This paper describes preparation of Al doped Zinc oxide thin film by sol-gel method. The films were prepared from the colloidal suspensions containing Al concentration and deposited on glass substrate by spin coating. Al doped films shows potential to increase in gas response of ZnO films. The response of the film is directly related to the surface area exposed.

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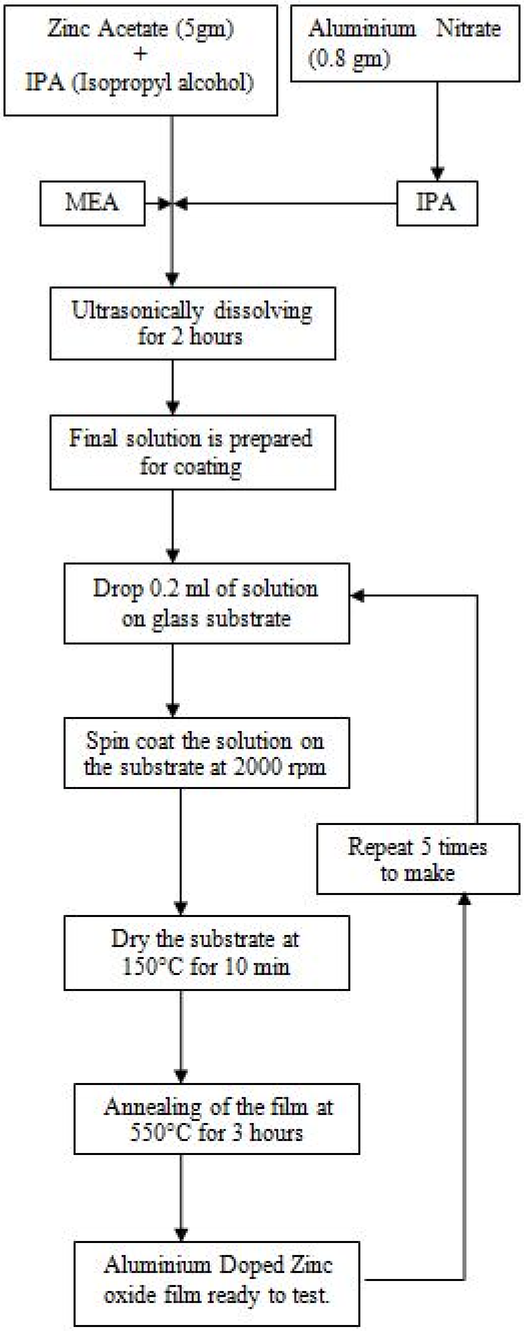

Fig. 1. Preparation steps of Sol-Gel mixture

II. Preparation of Sol-Gel Mixture

Fig. 1 shows the preparation of the thin film. Fig. 2 Shows the photograph of Al doped ZnO thin film sample. Precursor was prepared by using zinc acetate, isopropylalcohol, MEA (ethanolamine) and aluminium nitrate.

A. Procedure

(1) Zinc acetate dehydrate (5gm) was dissolved in isopropyl alcohol and then MEA was added drop by drop as the stabilizer.
(2) Aluminium nitrate (0.8gm) was added to the solution as the dopant material in ZnO.
(3) The final solution was placed in an ultrasonic bath at

Fig.2. Photograph of the Al doped ZnO Thin Film

room temperature for 2 hours.

B. Coating and calcinations of the Solution

(1) The glass substrate was washed and used. The sol-gel final mixture formed were spin coated on glass substrate at a rotation speed of 2000 rpm for 30s to ensure the sol-gel mixture spreads over the whole substrate surface uniformly.
(2) To remove the extra solvent and organic residuals, the coated films were preheated in furnace at 150æ%C for 10min.
(3) Final films were annealed in furnace at 550æ%C for 3 hours. For multilayer films the above process is repeated 5 times.

III. Characterization

Fig. 3 shows the XRD patterns of Al doped ZnO thin film . X-ray diffraction analysis was done from 20-80° with a step size of 0.1°/step (2è). It is indicated that ZnO thin film had a wurtzite structure according to the report in JCPDS file[6].The crystal size can be determined using [5]Debye Scherer's formula given by

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (2)$$

Where β= full maxima half width,θ = Diffraction angle, λ= wavelength (1.54 A°) and D= Crystal size. The Crystal size found out by above formula is 2.71μm.

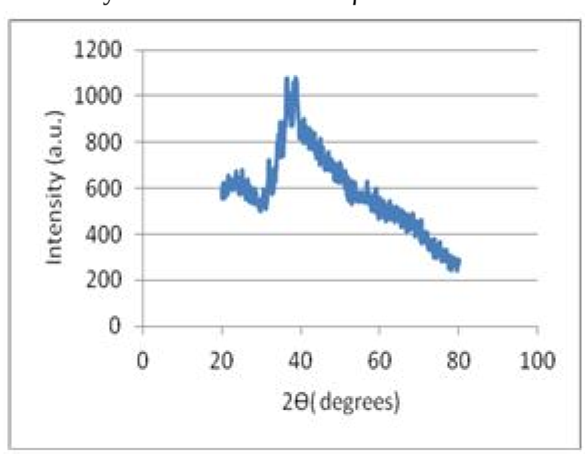

Fig.3. X-ray Diffraction patterns of Al doped ZnO thin film

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IV. Experimentation And Results

The resistance of the Thin film slide was observed at room temperature by using infrared thermometer (METRAVI MT4) and digital multimeter (DT9205A). Then the slide was put on the heating plate and resistance was measured at different temperature. Table 1 shows the resistance of the thin film at different temperatures. Resistance of the same slide was measured at room temperature by passing CO_2 gas over it. Then the slide was put on the heating plate and resistance was measured by varying temperature and passing CO_2 gas over it. Table 2 shows the resistance of the film at different temperatures when CO_2 gas was passed over it at 5 LPM and 2 bar pressure. Fig. 4 shows that the resistance of the thin film decreases with increase in temperature when CO_2 gas is passed over the thin film.

Table I. Resistance at various temperatures without CO2 gas passed over the Al doped ZnO thin film

Sr. No.	Temperature (°C)	Resistance without CO_2 gas passed (MΩ)
1	29.4	39.5
2	48	35.2
3	108	37.2
4	156	23.2
5	206	26.5
6	250	18.2
7	300	8.1
8	348	9.1

Table II. Resistance at various temperatures when CO2 gas passed over the Al doped ZnO thin film

Sr. No.	Temperature (°C)	Resistance with CO_2 gas passed (MΩ)
1	30.6	171.6
2	44	27.4
3	80	12.1
4	100	2.6
5	135	2.6
6	142	2.6
7	310	9

V. Conclusion

Al Doped ZnO thin films made by sol-gel method shows response to CO_2 gas. As the temperature of heating plate increases the resistance of the material decreases. The thin film prepared shows change in resistance as the temperature is varied. The resistance of the thin film further reduced at high temperature when CO_2 gas ispassed on the film. This shows that the Al doped ZnO thin film is sensitive to CO_2 at high temperatures. In this experimentation it is observed that the after a particular temperature i.e 300 æ%C the sensitivity to the CO_2 gas is reduced. It can be concluded that such a Al doped ZnO thin film is sensitive to CO_2 for a particular

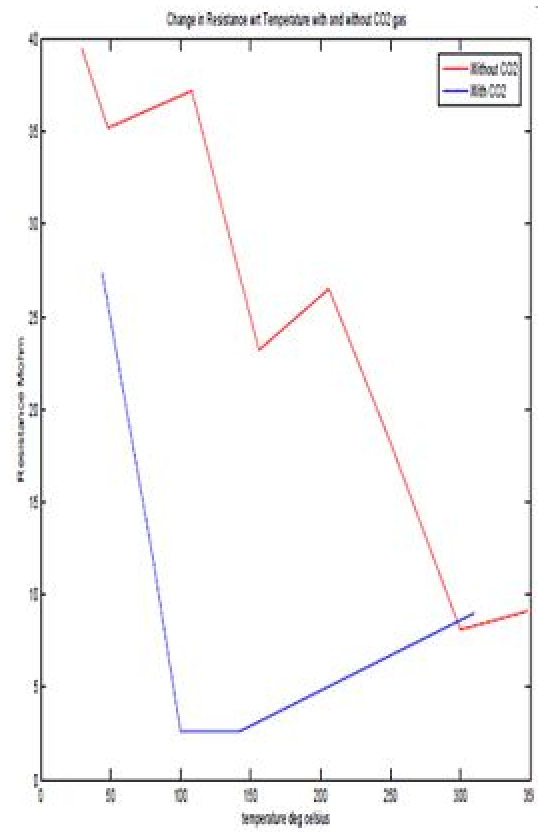

Fig. 4. Change in resistance wrt temperature with and without CO2 gas passed over Al doped ZnO thin film

temperature range say 50æ%C to 300æ%C. This Al doped ZnO thin film can be used for sensing a CO_2 gas in boiler flue gases.

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